FLUORESCENT MONITORING METHOD FOR POLYMERIZATION REACTIONS

BACKGROUND OF THE INVENTION

This invention relates to a method for measuring the physical-chemical kinetics of resin systems undergoing polymerization. Specifically, it relates to a method for monitoring the extent and determining the rate of cure of resin systems undergoing polymerization by incorporating into the resin system a fluorescent dye which reacts with the resin and changes the fluorescence in proportion to the extent of cure of the resin.

Polymerized resin systems are widely used in this and foreign countries for a variety of purposes. In general, any plastic structure, whether thermoplastic or thermosetting, is derived from a polymerized resin system.

Epoxy resins, for example, are commercially used in coating and structural applications. They are frequently used as fiber-reinforcing materials in the production of laminates and composites. Printed wiring boards used in electronic devices, in particular, are made from epoxy resin-based laminates or composites. Epoxies are used because of their hardness, resistance to corrosive environments, and relatively low dielectric constants.

The quality and properties of composite parts made from epoxy resins depend on several factors, including the proper cure of the epoxy resin. Variations in time and temperature, and polymer composition all affect the proper curing. Typically, the composites are cured for excessive lengths of time to insure the complete cure of the epoxy resin. The ability to monitor the epoxy curing process on line for the fabrication of composite parts would provide several advantages over existing methods. Correct cure cycles could be identified to prevent incomplete cure of the epoxy resin. Incomplete cure results in a loss of strength of the composite, a lack of uniformity in the physical characteristics, and undesirable variations in the dielectric constant. It also affects the thermal stability of the end product. The ability to identify correct cure cycles is especially important in the production of high-cost parts, where increasing the production rate while maintaining quality would be valuable In addition, part quality could be inspected by randomly sampling the extent of epoxy cure. Finally, the cure could be monitored in different regions of large or complex parts to insure homogeneous properties in the final product.

Epoxy resins are characterized by a 3-membered ring known as the epoxy, epoxide, oxirane, or ethoxylene group. These resins are prepared by the reaction of compounds containing an active hydrogen group with epichlorohydrin, followed by dehydrohalogenation. Optimum performance properties are obtained by cross-linking the epoxy resins into a three-dimensional insoluble and infusible network To accomplish this, the resin is treated with a curing agent or hardener The specific choice of curing agent or hardener depends on processing methods, curing conditions, and the specific physical and chemical properties desired. Primary and secondary amines are the most widely used curing agents for epoxy resins.

The structure and properties of epoxies are known to strongly depend on the extent of cure and physical aging which has taken place after the cure cycle is completed. The curing of a thermoset epoxy resin can be expressed in terms of a time-temperature-transformation relationship. There are normally considered to be four distinct states of the thermosetting-curing process: liquid, gelled rubber, ungelled glass, and gelled glass. The time-temperature-transformation diagrams can be used to establish chemical structure-physical property relationships of fully cured systems, since each system is unique in the kinetic before final cure and the physical properties it imparts. The extent of cross-linking is a measure of the degree of cure. The most favorable properties, i.e., high strength, thermal stability, chemical resistance, etc., are obtained by maximum cross-linking.

THE PRIOR ART

A number of physical chemical techniques have been used or developed to measure the degree of cure and physical aging in epoxies and other polymer systems. The two most widely used techniques to monitor epoxy cure at the present time follow first, sample temperature and second, dielectric properties during the cure process. However, there are disadvantages to using these techniques. The use of thermocouples to monitor the temperatures provides insufficient information of the cure. This is due to complicated heat transfer mechanisms of the system. Complex diconvolution routines are required to separate heat transfer phenomenon from actual sample temperature effects. Dielectrometry, although applicable for some processes, is limited because the sensors are too large to be included in a part. Furthermore, the sensors are expensive and are not feasible in use in high-volume applications. Other monitoring systems have been developed, although none are in commercial use at the present time.

U.S. Pat. No. 4,810,438, discloses a technique for controlling the curing process of fiber-reinforced composite materials that are formed using thermosetting resins. The technique is described as a percent gel method which involves development of a time-to-gel equation as a function of temperature. From this equation, a rate-of-gel equation is then determined, and a percent gel is calculated which is the product of rate-of-gel times time. The percent gel accounting is used to control the proper pressure application point in an autoclave cure process to achieve desired properties in a production composite part.

Levy et al., in an article in *Polym. Sci. Technol.* Plenum) 1984, 29, (Adhes. Chem.), pp. 245-56, describes the utilization of a viscosity-dependent fluorescence probe for in-situ monitoring of epoxy cure kinetics. In this method, the fluorescence emission spectrum of a probe-containing specimen is recorded at room temperature after each curing interval at the selected cure temperature. A parallel series of spectra is reported of an epoxy specimen which does not contain the fluorescence probe. The reference series of fluorescence emission spectra is recorded to ascertain that the observed increase of fluorescence results solely from increase of the fluorescence quantum yield of the probe. The fluorescence measurements are performed using a fluorometer. The fluorescence probe used is "polyester yellow" dye, one of a series of p-(N,N-dialkylamino)benzylidene malononitriles.

Another article by the same author in *Polym. Mater. Sci. Eng.* 1987, 56, pp. 169-74 describes a cure sensor which is based on the combination of fiber optic fluorometry and viscosity-degree of cure dependence of the resin fluorescence. The resin fluorescence observed in